



## Short communication

A high performance Ru–ZrO<sub>2</sub>/carbon nanotubes–Ni foam composite catalyst for selective CO methanationJun Xiong<sup>a,d</sup>, Xinfu Dong<sup>a,\*</sup>, Yibing Song<sup>b</sup>, Yingchao Dong<sup>c,\*\*</sup><sup>a</sup> School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, PR China<sup>b</sup> Chemistry Department, Shantou University, Shantou 515063, PR China<sup>c</sup> Environmental Ceramic Group, Institute of Urban Environment, Chinese Academy of Sciences, PR China<sup>d</sup> School of Pharmaceutical Sciences, Zunyi Medical College, Zunyi 563003, PR China

## H I G H L I G H T S

- A novel Ru–ZrO<sub>2</sub>/CNTs–Ni foam composite catalyst was prepared.
- CNTs–Ni foam composite, coupling merits of CNTs and Ni foam, was used as support.
- This catalyst exhibits excellent performances for selective CO methanation.

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## A B S T R A C T

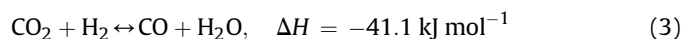
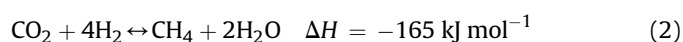
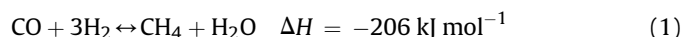
A novel Ru–ZrO<sub>2</sub>/carbon nanotubes (CNTs)–Ni foam composite catalyst for selective CO methanation is prepared by using CNTs–Ni foam as support. This catalyst exhibits an improved performance of CO selectivity and excellent catalytic stability, which may be attributed to the high thermal conductivity and unique microstructure of the Ru-based CNTs–Ni foam composite. The SEM and XRD measurements reveal that amorphous Ru–ZrO<sub>2</sub> particles with fine size (<20 nm) are well dispersed on the CNTs surface of the composite catalyst reduced at 350 °C, possibly leading to its high catalytic activity.

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## 1. Introduction

Proton exchange membrane fuel cell (PEMFC) with hydrogen as fuel is considered to play an important role in the future energy generation for transport applications as well as for stationary fuel cell applications and portable fuel cell applications, due to its high power density and zero emission [1–3]. The on board production of hydrogen from liquid hydrocarbon fuels provides a promising strategy for H<sub>2</sub> fed in fuel cell, yielding a hydrogen-rich gas mixture that contains considerable amounts of H<sub>2</sub>O, CO<sub>2</sub>, and CO [1,4]. However, pure Pt anodes of PEMFC are easily poisoned if the concentration of CO in H<sub>2</sub> fed is higher than 10 ppm [5–9]. Therefore, the purification step is required to decrease CO concentration to a very low level (<10 ppm) in hydrogen-rich gas mixture before

entering a fuel cell [10]. Although preferential oxidation of CO (PROX) is an effective way to decrease CO concentration to less than 10 ppm, this process requires an external oxygen (or air) supplier, a cooling system, and a mixer for hydrogen-rich gas and oxygen (or air), which may give rise to various problems related to hydrogen dilution, restrictions in the operation, thereby severely limiting its transport applications powered by PEMFC [1,4,6,7,11,12]. Thus, it is necessary to develop more feasible alternative approaches for CO “deep-cleaning” (<10 ppm) from hydrogen-rich gas mixture. Recently, some researchers have been being focused on selective CO methanation without any additional systems, which is a low-cost and space-saving substitute for PROX, because the necessary reactants (CO and H<sub>2</sub>) are already present [7,10–12].



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In selective CO methanation, as CO methanation reaction (Eq. (1)) occurs, CO<sub>2</sub> methanation reaction (Eq. (2)) and reverse water–gas shift reaction (RWGS) (Eq. (3)) may also take place, and the latter two reactions are undesirable from the viewpoints of hydrogen consumption, and CO removal from hydrogen-rich gas stream [4]. It is noted that the selective CO methanation process is sensitive to reaction temperature, because both CO<sub>2</sub> methanation and RWGS reaction can be retarded significantly at low reaction temperature (<250 °C) [4,10]. Thus, a high catalytic activity at low temperature is very important for the catalysts developed for CO selective methanation. Among them, ruthenium-based catalyst has been considered to be the most active one [4,7,10,13,14]. Takenaka et al. [4] reported that Ru/TiO<sub>2</sub> could decrease the concentration of CO from 0.5 vol% to 20 ppm in a narrow temperature range of 220–240 °C. In our previous work [13], Ru–ZrO<sub>2</sub>/carbon nanotubes (CNTs) catalyst presented a very high catalytic activity, reducing the CO concentration from 1.2 vol% to a very low level (<10 ppm) in the relatively wide temperature range of 180–240 °C. However, it is still a huge challenge to maintain a high selectivity for CO methanation during reaction [10,14]. The localized “hot spots”, caused by strong exothermic reactions of CO and CO<sub>2</sub> methanation, are responsible for a further increase in CO<sub>2</sub> conversion, reducing CO selectivity while increasing hydrogen consumption [14,15]. Consequently, it is of great importance to develop the catalysts with both high catalytic activity and high CO selectivity for selective CO methanation.

In this work, a novel Ru–ZrO<sub>2</sub>/CNTs–Ni foam composite catalyst for selective CO methanation was prepared by using CNTs–Ni foam composite as support, featuring the couple merits of CNTs and Ni foam. Our idea is that CNTs would well disperse active nano-sized Ru–ZrO<sub>2</sub> particles, assuring a high catalytic activity, while highly porous Ni foam skeleton offers high thermal conductivity and efficient micrometer-sized micro-channels for catalytic reaction, preventing the formation of localized hot spots and enhancing CO selectivity. Additionally, its three-dimensional (3D) network structure could enhance a diffusion-reaction process between reactants and surface active sites of Ru–ZrO<sub>2</sub> catalyst, ensuring a favorable catalytic performance [16].

## 2. Experimental

### 2.1. Catalyst preparation

A detailed synthesis process of CNTs–Ni foam composites is described in our previous work [17]. The diameters of the as-prepared CNTs were in the range of 20–65 nm, and the weight

fraction was 20%. Prior to the loading of active components, the CNTs–Ni samples were immersed in 0.5 M NaOH aqueous solution for 1 h, and then in 0.5 M HNO<sub>3</sub> aqueous solution for 45 min, followed by washing with deionized water, and finally dried sufficiently at 100 °C in an electrical oven.

The Ru–ZrO<sub>2</sub>/CNTs–Ni catalysts with 7 wt.% Ru loading (Ru/Zr = 1) were prepared by the wetness incipient impregnation method as follows: the CNTs–Ni foam supports were impregnated with an aqueous solution containing a given amount of RuCl<sub>3</sub> and ZrOCl<sub>2</sub>, followed by drying at 120 °C for 1 h, then washed with distilled water, and finally calcined at 180 °C for 2 h.

### 2.2. Catalyst evaluation

The selective CO methanation experiment was conducted in a micro-reactor at atmospheric pressure (see Fig. 1). The dimensions of the reaction chamber were 30 × 27 × 1.8 mm (*L* × *W* × *H*). The catalyst (about 400 mg) embedded into the chamber was first reduced with a mixed gas consisting of 20% H<sub>2</sub> and 80% nitrogen for 1 h at 350 °C, and then a gas mixture of 79.0% H<sub>2</sub>, 1.0% CO and 20.0% CO<sub>2</sub> was successively introduced into the reactor as the feed at a flow rate of 25 ml min<sup>−1</sup>. The effluent gas out of the reactor was sampled out and analyzed online by GC (Agilent 4890D) with TCD (thermal conductivity detector) and FID (flame ionization detector). The CO selectivity (*S*<sub>CO</sub>) is calculated according to the following formula:

$$S_{CO} = \frac{C_{CO}^{inlet} \times V_{inlet} - C_{CO}^{outlet} \times V_{outlet}}{C_{CH_4}^{outlet} \times V_{outlet}} \times 100\%$$

where *C*<sub>CO</sub><sup>inlet</sup>, *C*<sub>CO</sub><sup>outlet</sup>, *C*<sub>CH<sub>4</sub></sub><sup>outlet</sup>, are inlet CO concentration, outlet CO concentration and outlet CH<sub>4</sub> concentration, respectively; *V*<sub>inlet</sub>, *V*<sub>outlet</sub> are inlet and outlet flow rates, respectively.

### 2.3. Catalyst characterization

The microstructure and morphology of the Ru–ZrO<sub>2</sub>/CNTs–Ni catalysts were investigated by a 1530VP scanning electron microscope (SEM) operated at 20 kV and equipped with an Oxford Inca 300 energy dispersive X-ray (EDX) analysis unit. The X-ray diffraction (XRD) measurement was carried out on an XD-3 X-ray diffraction meter (Beijing Purkinje General Instrument Co., Ltd.) at 36 kV and 20 mA using Cu Kα radiation with 1.5406 nm of incidence wavelength. The XRD patterns were recorded in the 2θ range of 10–90° at a scan rate of 2° min<sup>−1</sup>.

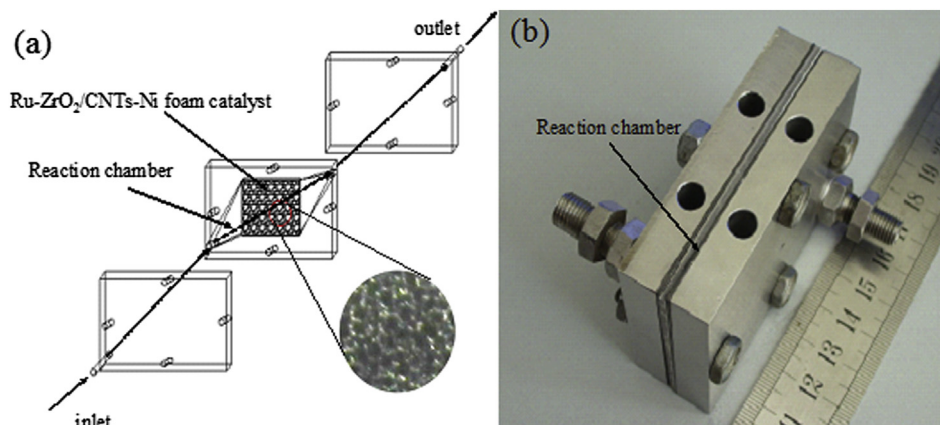


Fig. 1. (a) Sketched configuration of the used micro-reactor; (b) picture of an integrated micro-reactor.

### 3. Results and discussion

#### 3.1. Characterization of Ru–ZrO<sub>2</sub>/CNTs–Ni foam composite catalyst

Fig. 2a shows a typical photograph of the as-prepared Ru–ZrO<sub>2</sub>/CNTs–Ni foam composite catalyst. After reduction with hydrogen gas at 350 °C, the active Ru–ZrO<sub>2</sub> particles with very small size (less than 20 nm) were well dispersed the surfaces of loaded CNTs (diameter: 20–65 nm), as shown in Fig. 2b. The corresponding EDX result during the SEM observation indicates that the tested sample had a nominal composition of C, O, Zr, Ru and Ni elements (see Fig. 2c).

The existence of Ru and ZrO<sub>2</sub> in this composite catalyst was confirmed by the XRD analysis. Fig. 3 shows the XRD patterns of the Ru–ZrO<sub>2</sub>/CNTs–Ni catalysts reduced at different temperatures from 350 to 550 °C. The peaks corresponding to nickel and graphite are present in all the samples [18–21]. No diffraction peaks of Ru and ZrO<sub>2</sub> were observed in the XRD pattern of the catalyst reduced at 350 °C, revealing the presence of amorphous Ru and ZrO<sub>2</sub>, which is similar to those observed by other researchers [13,22]. After reduction at the temperatures above 450 °C, the diffraction peaks corresponding to metallic Ru and t-ZrO<sub>2</sub> appear [23–26], indicating the crystallizations of Ru and t-ZrO<sub>2</sub>.

#### 3.2. Selective CO methanation performance over Ru–ZrO<sub>2</sub>/CNTs–Ni foam composite catalyst

Fig. 4 shows the outlet concentration (open symbols) and CO selectivity (filled symbols) as a function of reaction temperature for CO selective methanation over the Ru–ZrO<sub>2</sub>/CNTs–Ni foam

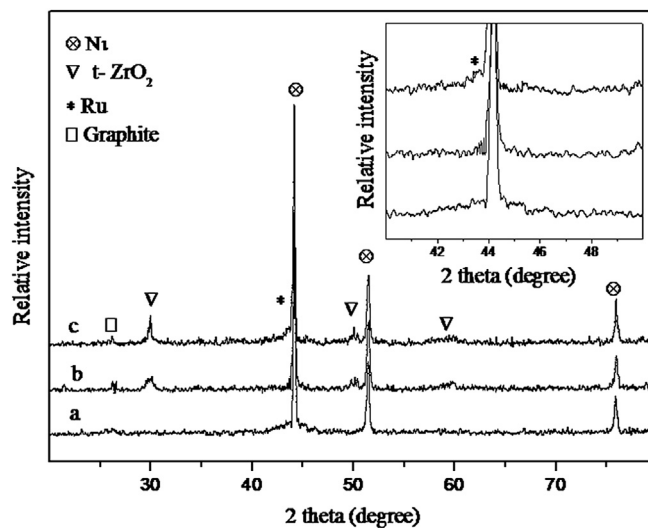


Fig. 3. XRD patterns of the Ru–ZrO<sub>2</sub>/CNTs–Ni foam composite catalysts reduced at different temperatures: (a) 350 °C; (b) 450 °C; (c) 550 °C. The insetted image shows a variation in the intensity of Ru peak with temperature.

composite catalysts reduced at various temperatures. For all the catalysts examined, the CO outlet concentrations first decrease with increasing reaction temperature (especially between 160 and 220 °C), then reach a minimum, finally increase gradually with the further increasing reaction temperature due to the competitive reactions of RWGS and CO<sub>2</sub> methanation [14,27]. This suggests that

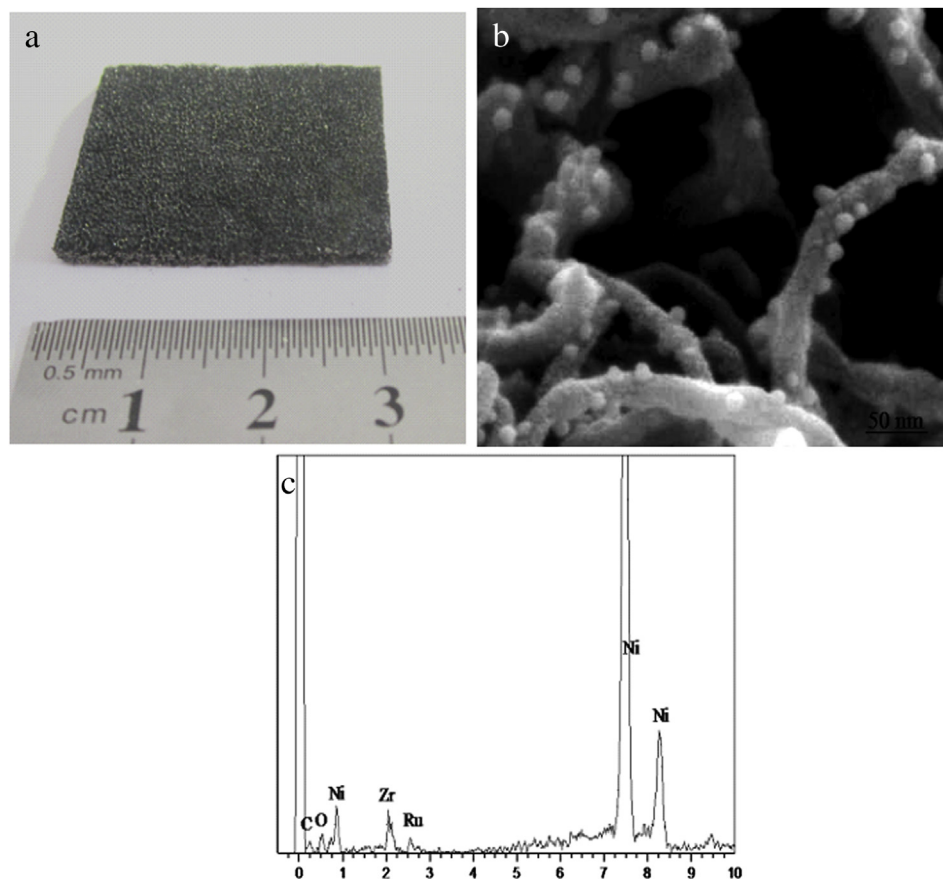


Fig. 2. (a) Photograph, (b) SEM image and (c) EDX spectrum of the Ru–ZrO<sub>2</sub>/CNTs–Ni catalyst.

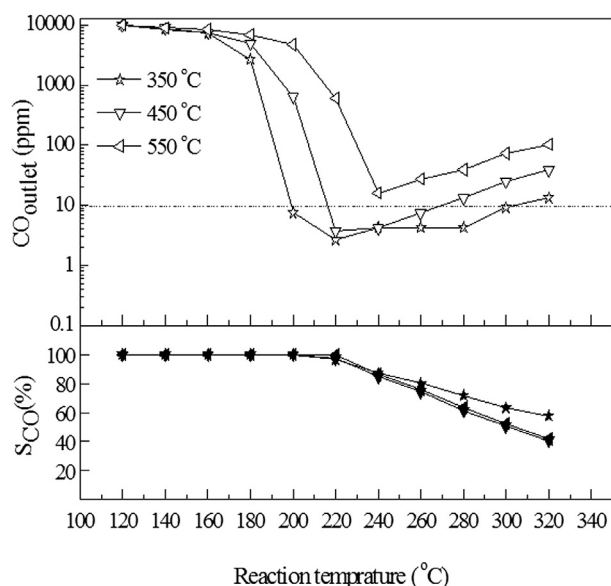


Fig. 4. Outlet concentration (open symbols) and CO selectivity (filled symbols) as a function of reaction temperature in selective CO methanation over the Ru–ZrO<sub>2</sub>/CNTs–Ni foam composite catalyst reduced at various temperatures.

the operating temperature window of catalysts reduced at different temperatures can be found, where the CO outlet concentrations are low enough (<10 ppm) for potential application in PEMFC, before CO levels rise too much. It is found that the catalyst reduced at 350 °C exhibits excellent performance, with a very wide temperature window between 200 and 300 °C, where the CO level is less than 10 ppm and keeping CO selectivity higher than 60%. Compared with the results of the conventional Ru-based catalysts reported previously [4,13,14], this Ru–ZrO<sub>2</sub>/CNTs–Ni foam composite catalyst has a wider temperature window where the CO level is less than 10 ppm and higher CO selectivity. However, with increasing reducing temperature to 450–550 °C, the catalytic performance of Ru–ZrO<sub>2</sub>/CNTs–Ni foam composite catalyst degraded gradually,

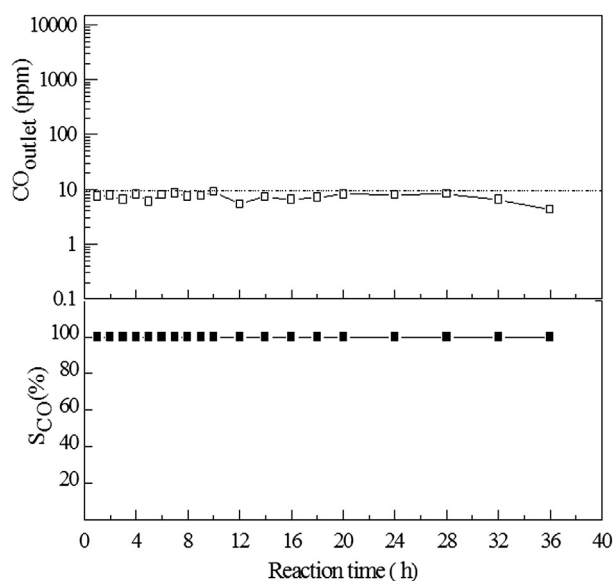


Fig. 5. Outlet concentration (open symbols) and CO selectivity (filled symbols) as a function of reaction time in selective CO methanation over the Ru–ZrO<sub>2</sub>/CNTs–Ni foam composite catalyst reduced at 350 °C.

due to the crystallization of amorphous active Ru component (see Fig. 3). This indicates that amorphous Ru is responsible for better catalytic properties than its crystallized form in CO selective methanation.

To confirm the catalytic stability of Ru–ZrO<sub>2</sub>/CNTs–Ni foam composite catalyst, a durability test was carried out by measuring CO outlet concentration and CO selectivity as a function of reaction time at the optimized reaction temperature of 200 °C. As shown in Fig. 5, the CO outlet concentration remains a level below 10 ppm and the CO selectivity keeps an extremely high value of 100% during a total reaction time of 36 h, indicating a good catalytic stability of this catalyst.

In the summary, the amorphous Ru–ZrO<sub>2</sub> particles with fine size (<20 nm) are well dispersed on the CNTs surface of the Ru–ZrO<sub>2</sub>/CNTs–Ni foam composite catalyst, and this composite catalyst has high thermal conductivity and sufficient porosity, which enhanced heat transfer, thereby making contribution to a good catalytic activity and stability.

#### 4. Conclusions

The Ru–ZrO<sub>2</sub>/CNTs–Ni foam composite catalysts were synthesized by wetness incipient impregnation and then successfully applied for the CO “deep-cleaning” (<10 ppm) process for hydrogen-rich gas stream via selective CO methanation. It was found that this amorphous Ru-based composite catalysts reduced at 350 °C present a good CO selectivity, excellent catalytic activity and stability, significantly decreasing CO concentration to below 10 ppm from 1% in a wide reaction temperature ranging from 200 to 300 °C, while keeping CO selectivity higher than 60%. Moreover, the durability test indicates that this catalyst has an outstanding catalytic stability, keeping an extremely high CO selectivity of 100% at 200 °C, which makes it to be a promising composite catalyst candidate for potential applications in PEMFC.

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